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Characterization of Self-Assembled SnO₂ Nanoparticles for Fabrication of a High Sensitivity and High Selectivity Micro-Gas Sensor

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ABSTRACT

In order to refine further the material technology for tin-oxide based gas sensing we are exploring the use of precision nanoparticle deposition for the sensing layer. Layers of SnO₂ nanoparticles were grown on Quartz Crystal Microbalance (QCM) resonators using the layer-by-layer self-assembly technique. Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM), and Electron Diffraction Pattern (EDP) analyses were performed on the self-assembled layers of SnO₂ nanoparticles. The results showed that SnO₂ nanoparticle films are deposited uniformly across the substrate. The size of the nanoparticles is estimated to be about 3-5 nm. Electrical characterization was done using standard current-voltage measurement technique, which revealed that SnO₂ nanoparticle films exhibit ohmic behavior. Calcination experiments have also been carried out by baking the substrate (with self-assembled nanoparticles) in air at 350°C. Results show that 50%-70% of the polymer layers (which are deposited as precursor layers and also alternately in-between SnO₂ nanoparticle monolayers) are eliminated during the process.

INTRODUCTION

Solid-state gas sensors find applications in automobiles, toxic and domestic environments, the chemical industry, and elsewhere. The gas-sensor market is fast burgeoning and was estimated to be about \$0.9 billion at the end of the last decade [1]. Ceramic SnO₂ has been used extensively as a sensor element in semiconductor gas-sensors for detecting a range of gases such as carbon monoxide, oxides of nitrogen, hydrogen sulfide, freon and many others [2]. SnO₂ is the prime choice for semiconductor sensors because of its bulk-material stability and resistivity characteristics. Sensors with SnO₂ as sensing element function on the principle of surface chemical reaction between an analyte gas and the sensing element, which causes a change in the resistance of the element. Thus the sensing characteristics depend on the surface properties of the element [3]. While performing sufficiently for commercial deployment, these sensors displayed a variety of material issues including the degree of crystallinity of SnO₂, crystallite size, density of lattice defects, surface area, and surface structure. These issues translated to low or varying selectivity and sensitivity of the SnO₂ sensors. Some of the techniques that have been implemented for improving the selectivity include cyclic manipulation of the sensor temperature, doping of the SnO₂ with various additives like Pt and noble metals [3], surface modification of the base metal oxide with hydrophobic groups, calcium oxide, zinc oxide and sulfur [4]. The

method of fabrication is also a variant in the process to improve the performance of SnO_2 sensors. The different routes for fabrication adopted for metal-oxide thin film sensors are sol-gel method of deposition of SnO_2 thin films, reactive sputtering [5], and sintering and annealing [6]. These fabrication methodologies attempted to deposit thin films of SnO_2 for manifesting improved selectivity and sensitivity. Decreasing the particle size of SnO_2 is another factor which could contribute to improving performance. In the present study, we attempt to circumvent many of the limitations of the traditional preparation methods by depositing SnO_2 nanoparticles using the Layer-By-Layer (LBL) self-assembly technique which is based on alternate adsorption of oppositely charged components [7].

Nanocrystalline structure is known to impart high sensitivity and selectivity to gas-sensors [8]. Nanoparticles offer a high degree of structural control due to their well-defined size and shape, and the LBL assembly method allows them to be uniformly and precisely ordered on the substrate with the precision of a few nanometers [9]. We therefore anticipate the resulting films to possess high reproducibility of thickness, of crystallite size, and of the geometry of intergranular contact, which are known to be key factors in the gas sensing mechanism [8]. In addition, the LBL process permits the architecture of the layer to be engineered by insertion of monolayers of alternate materials (e.g. SiO_2 to enhance activity), doped nanoparticles, or nanoparticles of varying radius to modulate the film density [4]. We report here on the characterization of the SnO_2 layers formed by the LBL method. SEM, TEM, and EDP analysis were done on the nanolayers of SnO_2 , in order to determine the size of the nanoparticles and thickness of the nanofilm. Electrical characterization was done to observe the current-voltage characteristics of the nanofilms. Calcination studies were also performed to investigate the elimination of the polymer layer, which is a by-product of the LBL process.

EXPERIMENTAL DETAILS

SnO_2 nanoparticles were obtained from Nyacol[®] NanoTechnologies (Nyacol Colloidal Tin Oxide) as two separate samples, SN-15 (negatively charged, pH 8.0-9.0, specific gravity 1.15, viscosity 5-10 cps and counter-ion concentration of 0.5% potassium) and SN-15CG (negatively charged, pH 9.0-10.5, specific gravity 1.15, viscosity 5-10 cps and counter ion concentration of 0.23% NH_3). The polyions used were Polydiallyldimethyldiammonium chloride (PDDA), Sodium-polystyrene sulfonate (PSS), and Polyethyleneimine (PEI) of 2 mg/mL in aqueous solution (all Sigma-Aldrich, [9]). The initial characterization of the SnO_2 was carried out on a quartz crystal microbalance (QCM, USI-System, Japan) resonator in order to monitor the film growth during each step in the process. The technique initially involves layer-by-layer electrostatic assembly of several pairs of oppositely charged polyion layers as the precursor layers to promote the structural stability of the subsequently assembled nanoparticles. The outermost precursor polyion layer is oppositely charged (positive) with respect to the anionic nanoparticles. Then the nanoparticles and the complimentary polyion layer are alternately self-assembled as shown in Figure 2.

Self-assembly was tried first with $\text{PEI/PSS}/(\text{PEI/SnO}_2)_7$ and then with $\text{PDDA/PSS}/(\text{PDDA/SnO}_2)_{7-16}$. The latter sequence was found to result in more reproducible growth of SnO_2 nanoparticle multilayers. Thereafter all self-assembly experiments were done with the same sequence, i.e., $\text{PDDA/PSS}/(\text{PDDA/SnO}_2)_7$. In order to assess whether steady-state conditions had been reached during the adsorption process, the time of retention of the QCM resonator in the SnO_2 colloidal solution was varied and the results were obtained as change in

frequency plotted against the number of monolayers assembled. The self-assembled samples were sent to RIKEN Frontier Research System, Topochemical Design Laboratory in Japan for SEM analysis. For TEM analysis for nanoparticle size measurement, EDP, and High Resolution TEM of nanoparticle grain structure, the samples were sent to Material Characterization Lab at Louisiana State University.

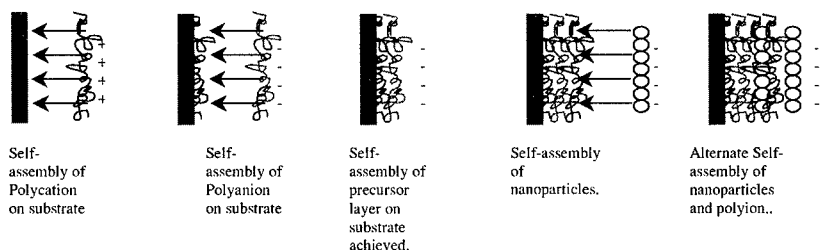


Figure 1: Schematic of the Layer-By-Layer process used for self-assembly of SnO_2 nanoparticles.

I-V characteristics were studied using a standard electrical characterization set-up. The samples were prepared as $2.75\text{cm} \times 3.5\text{cm}$ coupons of Pyrex glass. SnO_2 nanoparticles were self-assembled on the glass substrate. Electrical contact patterns were designed using LEDIT[®] software. The pattern was transferred onto Mylar[®] sheets, and cut out to form electrical contact patterns. Patterns for both two-point and four-point tests were created. Using these patterns, Pt contacts were sputter deposited onto the self-assembled glass samples. The samples were then tested for their I-V characteristics.

Calcination studies were carried out by baking a blank silver electrode resonator (resonator with no self-assembled layers), and another with 20 self-assembled layers of SnO_2 in a Thermolyne[®] Furnace at 350°C for 4 hours in one-hour intervals. The frequency readings for both the resonators were taken after each hour interval.

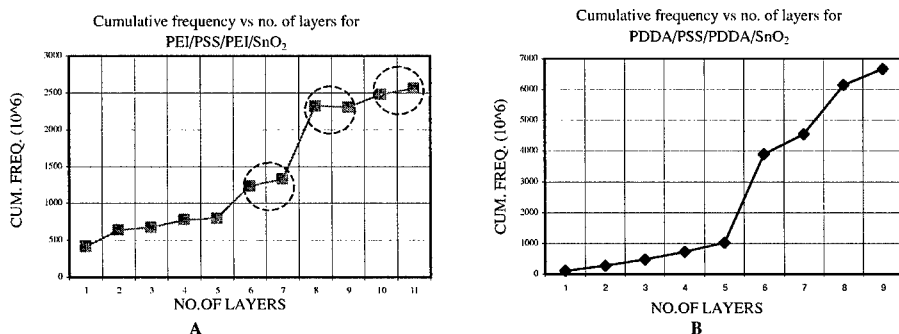


Figure 2: Graphs for cumulative ΔF (Hz.) for (A) $[\text{PEI}/\text{PSS}/\text{PEI}/\text{SnO}_2]$ and (B) $[\text{PDDA}/\text{PSS}/\text{PDDA}/\text{SnO}_2]$.

RESULTS AND DISCUSSION

Self-Assembly of SnO₂ Nanoparticle Multilayers and Characterization

SnO₂ nanoparticles were self-assembled on a QCM resonator using two alternative sequences: 1) PDDA/PSS/ (PDDA/SnO₂)_n and 2) PEI/PSS/(PEI/SnO₂)_n, where n = 5-16. After every adsorption cycle, a sample was dried, and the QCM frequency was measured. The frequency shifts (ΔF) characterized the mass adsorbed on resonator, and an increase of the film thickness [3].

As seen in the Figure 2 (A), the three-circled areas represent poor or irreproducible uptake of the PEI layer. This irreproducibility led to non-uniform deposition of subsequently self-assembled SnO₂ nanoparticle layers. No such phenomenon is observed in the sequence PDDA/PSS/PDDA/SnO₂. Therefore it was concluded that the second sequence was better suited for self-assembly of SnO₂ nanoparticles as it exhibited sound linearity in growth characteristic. Further experiments were carried out with the sequence PDDA/PSS/PDDA/SnO₂ and the time of immersion in the SnO₂ colloidal nanoparticle solution was varied from 20 minutes, 10 minutes, and 15 minutes down to 5 minutes. Figure 3 shows that the self-assembly of SnO₂ follows an approximately time-independent behavior i.e. addition of nanoparticles is essentially complete in less than 5 minutes of immersion time. This behavior yields a high precision of thickness control in the growth process. The anomalous behavior in the 18th growth layer of the 20-minute immersion film can be attributed to manual errors in handling the resonator while transferring it from one solution to another and/or handling while drying.

High-resolution imaging reveals that the particle size is approximately in the range of 3-5 nm. The thickness of the film deposited was calculated to be 490 nm using the QCM frequency data and the relation $\Delta t = -0.016 \cdot \Delta F$ [9] and the results obtained from the SEM analysis show that the thickness of the self-assembled films of eight SnO₂ monolayers is approximately 300-400 nm.

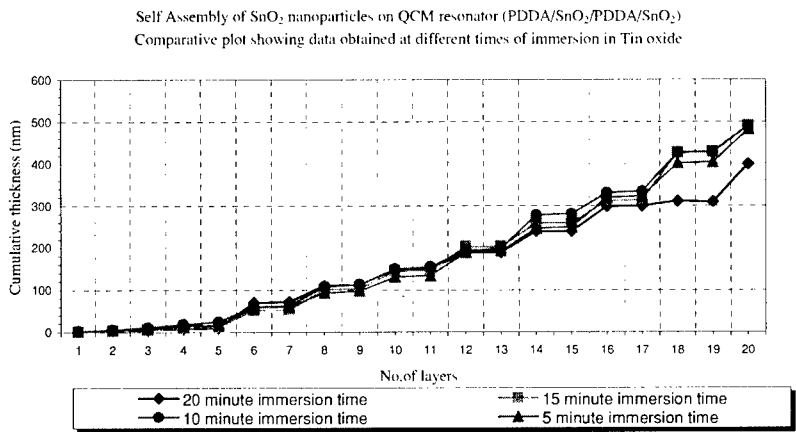


Figure 3: Comparative plot showing data obtained at different times of immersion in tin-oxide colloidal nanoparticle solution.



Figure 4: SEM image of cross-section of QCM resonator with self-assembled SnO₂ nanoparticles.

Electrical Characterization

Coupons of Pyrex glass of the same dimensions as the electrical patterns were prepared and Pt contacts 2000Å were sputter coated onto the coupons. One coupon was calcined for 1 hour to eliminate interlayer polyions. Two-point I-V results showed linear (ohmic) behavior of the deposited SnO₂ layers (Figure 5) for the calcined sample. The I-V characteristics for the uncalcined sample showed several spurious readings which are linked to the presence of the polyion layers in between the SnO₂ nanoparticle layers. We believe polyion layers impose regions of parallel conductance that undergo electrical breakdown to a high-impedance state thereby resulting in what appears to be a I-V characteristic superimposed with noise. Measured resistivities were 0.18 ohm-cm for the uncalcined sample, and 0.63 ohm-cm for the calcined sample.

Calcination

Calcination effectively eliminates the spurious points and also results in a higher net resistivity corresponding to the substantial reduction in polyion conductivity contribution. In the first calcination experiment, a self-assembled QCM resonator with 8 layers of SnO₂ (and total of 20 layers including the polyion layers), and a blank resonator control were used for

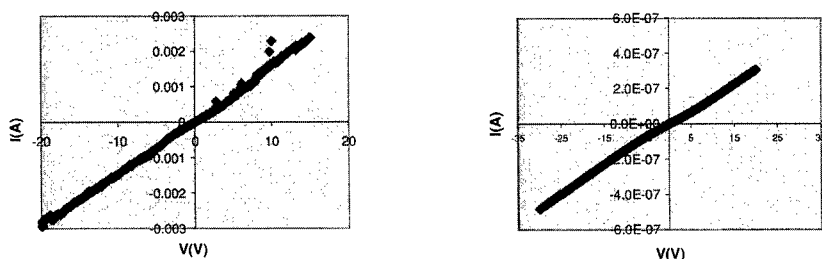


Figure 5: I-V characteristics for uncalcined (left) and calcined (right) samples.

calcination studies. Both the resonators were calcined for 4 hours and frequency measurements were recorded after every 1-hour interval. The initial frequency was measured for both the resonators before calcination. After every 1 hour, frequency deviation was recorded for both the resonators. Mass change was calculated using the relation [3]:

$$\Delta m(\text{ng}) = -0.87 \cdot \Delta F(\text{Hz}) \quad (1)$$

The self-assembled resonator lost approximately 2000 ng in the first hour, and less than 300 ng thereafter. The initial loss corresponded to 50% loss of total polyion deposited by self-assembly.

These results are in agreement with earlier study of temperature decomposition of the linear polycation / polyanion multilayers [10] which have shown that calcinations at 350° C for three hours is necessary to eliminate these films.

CONCLUSION

We have demonstrated self-assembly of SnO₂ nanoparticles on QCM resonator and glass substrates. SEM, TEM, and HRTEM analysis have been performed which give an estimate of the SnO₂ nanoparticle size, which is approximately 3-5 nm. The SnO₂ nanoparticle films deposited by LBL process are uniformly deposited across the substrate and the thickness of these films can be precisely controlled. Electrical characterization of self-assembled SnO₂ substrates has been performed and results show that self-assembled samples, which are calcined, show smoother ohmic behavior as compared to self-assembled samples, which are not calcined. Preliminary calcination studies show that approximately 55% to 70% of polyion mass is eliminated in the process.

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